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Development of a 3D printable maxillofacial silicone: Part I. Optimization of polydimethylsiloxane chains and cross-linker concentration

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## ABSTRACT

**Statement of problem.** Traditionally, maxillofacial prostheses are fabricated by hand carving the missing anatomic defect in wax and creating a mold into which pigmented silicone elastomer is placed. Digital technologies such as computer numerical control (CNC) milling and 3-dimensional (3D) printing have been used to prepare molds directly or indirectly into which a biocompatible pigmented silicone elastomer is placed.

**Purpose.** The purpose of this in vitro study was to develop a silicone elastomer by varying composition that could eventually be 3D printed directly without a mold to create facial/body prostheses.

**Material and methods.** The silicone was composed of polydimethylsiloxane (PDMS), filler, catalyst, and cross-linker. Four types of base silicone polymers were prepared with different PDMS molecular weight combinations with long, medium, and short chain length PDMS. The effect was assessed of 2.5% to 12.5% cross-linker content in these bases on the mechanical properties of the elastomer. Ten readings were made for each formulation, and differences in the means were evaluated with a 2-way ANOVA ( $\alpha=.05$ ).

**Results.** The variations in silicone composition resulted in hardness from 6.8 to 28.5 durometer Shore A, tensile strength from 0.720 to 3.524 kNm<sup>-1</sup>, and tear strength from 0.954 to 8.484 MPa. Significant differences were observed among all formulations ( $P<.05$ ). These formulations have mechanical properties comparable with the commercial silicones currently used for the fabrication of facial prostheses. The formulation with 5% cross-linker content and high content of long-chain PDMS chains with optimum mechanical properties was chosen for further development.

**Conclusions.** The optimum combination of mechanical properties implies the use of one of these formulations for further evaluation in a 3D printer capable of actively mixing and extruding 2-component, room temperature vulcanization (RTV) silicone.

## CLINICAL IMPLICATIONS

The direct 3D printing of biocompatible silicone prostheses will make the process of manufacturing a more reproducible, consistent, and reliable process. This will also reduce

healthcare costs in terms of chair time and the number of appointments and permit replacement prostheses to be produced more rapidly.

## INTRODUCTION

Maxillofacial prostheses are used to replace missing facial/body tissues that have been lost through congenital malformation, disease, surgery, or trauma. These defects may be compensated for by pigmented silicone elastomers that closely resemble the natural surrounding tissues. The method of fabricating facial prostheses has essentially remained unchanged for many decades and is considered by some to be an art form.<sup>1</sup> It depends upon the artistic skills of the maxillofacial prosthetist or anaplastologist and their interpretation of replacing the missing defect, with varying degrees of success. The whole process of fabrication of the prosthesis is time consuming and not easily reproduced.<sup>2-4</sup>

Traditionally, facial prostheses are fabricated by recording an impression of the affected tissue, hand carving the missing defect, creating a 2- or 3-part mold into which pigmented silicone which is visually color matched to the surrounding tissue is placed.<sup>2,5,6</sup> Several technologies are available, and now anatomic casts or molds can be made digitally with hard resins. As an alternative to recording an impression stereophotogrammetry is used to capture 3D surface data which can be used to design prostheses digitally with computer-aided design (CAD) programs. These designs can be 3-dimensionally (3D) printed in metal, plastic, resin, paper, or even hard rubber, but their use is limited for prostheses as most of them are hard and hence unsuitable. They do not mimic the soft tissue they would replace if used directly as prostheses. Furthermore, prostheses need to be individually color matched to each patient. Several groups use these technologies to make molds directly or indirectly and then manually pack them with pigmented silicone to fabricate prostheses.<sup>5, 7-10</sup>

Silicone rubbers are the current material of choice for the fabrication of prostheses, offering good mechanical properties and durability. They are physiologically inert, chemically resistant, thermostable over a wide range of temperatures, and biocompatible.<sup>11</sup> The most common silicone rubber used in maxillofacial prostheses is based on a polydimethylsiloxane polymer (PDMS) with a surface treated silica filler, catalyst, and cross-linker. By varying the amount of these components, the mechanical properties of the silicone elastomer can be altered, including its tensile strength, tear strength, hardness, and wettability.<sup>12-14</sup> In general, silicone elastomers can be classified into 2 major categories depending upon the polymerizing or setting reaction of the cross-linker with PDMS chains: either heat vulcanizing or room temperature vulcanizing (RTV).<sup>6</sup>

For heat vulcanizing silicones, the mixture of ingredients is heated to activate the catalyst/cross-linker to form an elastomer, while for RTV silicones, this is not necessary. Depending upon the catalyzing reaction, RTV silicones can be subdivided into 2 types: 1- and 2-component RTV silicones. Two-component RTV silicones consist of 2 parts, the cross-linker is separated from the component until the final polymerization step. As the cross-linker comes into contact with the other component it induces polymerization. A 1-component RTV silicone is kept in a sealed container as exposure to moisture in the air causes vulcanization through volatilization of acetic acid.<sup>6</sup>

The chosen 3D printing method was based on extruding the unpolymerized silicone elastomer through a cylindrical deposition nozzle onto an unheated substrate in a controlled, layer-by-layer pattern. For this method, the silicone should possess characteristics of consistent flow through a deposition head with modest pressure, retention of the extruded shape without significant slumping, controllable polymerizing rate, and mechanical properties comparable with

existing clinical silicones. RTV silicone systems using unmasked platinum catalyst rapidly polymerize silicone without the application of heat. Although, 1-component RTV silicones can be 3D printed, 2-component RTV silicones are preferable for prostheses because of their biocompatibility.<sup>15</sup> In this paper, we focus on testing the mechanical properties of heat-polymerized silicone formulations. The purpose of this study was to develop a silicone with the desirable properties of commercially available silicones and ultimately suitable for manufacturing facial prostheses with 3D printing. This paper describes the optimization of the mechanical strength of the silicone by altering PDMS chains and cross-linker without consideration of the working time.

## **MATERIAL AND METHODS**

Although, heat-polymerizing silicones cannot be used for 3D printing, they do have the advantage of a working time of 30 minutes or more. In order to develop the ideal properties required for the maxillofacial material, a heat catalyst was initially chosen for ease of workability in development. This will be replaced by a RTV catalyst at a later stage in the development when mechanical properties are already optimized.

Each formulation consisted of 3 PDMS chains, 20% of 1 surface treated filler (hexamethyldisilazane treated fumed silica), 1 cross-linker (methylhydrosiloxane – dimethylsiloxane copolymer - HMS301), and 1 heat catalyst (platinum carbonyl cyclovinylmethylsiloxane complex). The commercial materials used as controls in the study were M511 and Z004 (Cosmesil; Technovent Ltd).

For the preparation of the polymeric bases, 3 polymers, long, medium, and short chain PDMS denoted by X, Y, and Z were used and were individually loaded with 20% wt/wt silica

filler (Table 1). The 4 base polymers prepared were made of all these 3 PDMS chains in varying ratios as stated in Table 2.

These bases were mixed with various cross-linker (HMS301) concentrations: 2.5, 5, 7.5, 10, and 12.5% wt/wt. The formulations were mixed with 2.5% catalyst (platinum carbonyl cyclovinyldimethylsiloxane complex) and speed mixed at 2000 rpm for 30 seconds (DAC 150FVZ-K; Speedmixer) to remove any air bubbles. Speedmixing was repeated if air bubbles remained within the formulated silicone elastomer. When it was considered bubble-free, it was packed carefully into molds using conventional methods to avoid entrapping air bubbles. The specimens were then polymerized at 85°C for 1 hour in a dry oven. After polymerizing, the specimens were removed from the molds, excess silicone was trimmed, and specimens were incubated at  $23 \pm 1^\circ\text{C}$  for 24 hours; their mechanical properties were then tested. Hardness, tear strength, and tensile strength test specimens were prepared for each of the formulations. Specimens with air bubbles after polymerization were rejected, and only air-free specimens were selected for testing.

For tensile testing, 10 type 2 dumbbell-shaped specimens were fabricated for each formula and tested according to ISO37.<sup>16</sup> The thickness of the dumbbell-shaped specimens was 2 mm. The specimens were tested at a strain rate of 100 mm/min with a universal testing machine (Model 5569A; Instron). Ten trouser-shaped tear test specimens were fabricated for each formula (100×15×2 mm) and tested according to ISO34.<sup>17</sup> A cut in the test specimen was made at the center of the width of the test piece (40 mm long). The specimens were tested at a strain rate of 100 mm/min with the universal testing machine (Model 5569A; Instron). Six hardness test specimens (40×25×8 mm) were made with a conventional dental flasking technique for each



formula, with each specimen measured once using a Shore A durometer (HBA 100-0; Sauter). The hardness test used a rigid ball indenter according to ISO868.<sup>18</sup>

The data were analyzed with software (Stata v14.1; StataCorp LP) ( $\alpha=.05$ ). The effects of base (4 levels) and cross-link concentrations (5 levels) on tear strength, tensile strength and hardness were tested with a 2-way analysis of variance (ANOVA) with an interaction term. The normality of residuals, an assumption for a valid ANOVA, was tested graphically using normal probability plots in conjunction with the procedure described by Cox.<sup>19</sup>

## RESULTS

The 4 prepared bases mixed with 5 cross-linker concentrations resulted in 20 formulations. Each of these was tested for hardness, tear, and tensile strength. The results of the analysis are summarized in Tables 3 for the main effects and in Figures 1-3 for the interactions. Slight deviations from normality were found at the tails of the data distributions but were not high enough to invalidate the ANOVA. The Sidak method was used to adjust for multiple comparisons ( $P>.05$ ). The tensile strength and hardness of all bases are significantly different but tear strength of Base B and C are not significantly different. Hardness values of formulations for all cross-linker concentrations are significantly different although the tensile strength at 2.5%, 7.5% and 10 % cross-linker are not statistically different. The tear strength of formulations 2.5% cross-linker concentration are not significantly different from 5% and 7.5% as well as 10% and 12% cross-linker concentration are not significantly different from each other for all bases. The interaction plots show the 95% confidence intervals.

The tensile strength (Fig. 1) of formulations with bases A (3.524 MPa) and B (2.212 MPa) peaked with the 5% cross-linker, base C (2.814 MPa) peaked at 2.5%, while base D (2.003

MPa) peaked at 7.5%. Base A and B showed an escalation in tensile strength with an increase in cross-linker from 2.5% to 5% and a drop in tensile strength at 7.5% cross-linker, after which it rose again at 10% cross-linker. A decrease in tensile strength was noted when cross-linker increased from 10% to 12.5% with all the bases. The formulation of Base A with 5% had the statistically highest tensile strength ( $P>.05$ ).

The analysis of tear strength of all formulations (Fig. 2) shows Base A had a higher strength than the other bases at all cross-linker values. Base D has very low tear resistance, even with high cross-linker. Overall, the formulations were strongest with 5% cross-linker and gradually weakened with the addition of more cross-linker.

Hardness fell with the increment of short chains in the base from base A to D (Fig. 3). For base A and B, hardness fell gradually with increasing cross-linker, but, for base C and D, it peaked at 5% cross-linker and fell afterward. Base D with 5% cross-linker had statistically the highest hardness ( $P>.05$ ), 28 durometer Shore A.

The hardness, tensile strength, and tear strength values for commercial silicones (M511 and Z004) are given in Table 4. Durometer Shore A hardness of M511 was 18.7 while Z004 had a shore hardness of 30.83. M511 also had lower tear and tensile strength than Z004. The mechanical properties of bases with 5% cross-linker loading listed alongside commercial silicones provide a comparison (Table 4).

## DISCUSSION

The purpose of this study was to develop a new silicone for 3D printing. The first step in the process was to optimize the cross-linker and PDMS chain length combination and concentration as this will affect the mechanical properties. The elastomers for use as maxillofacial materials

have a balanced combination of high tensile strength and elongation at break, tear strength, and hardness within the favorable range. The mechanical strength of the prosthesis is a major concern; therefore, various mechanical tests were performed on the selected formulations and commercial silicones. For prostheses, high tensile strength is an advantage in that it can withstand high tensile loads and has a high yield point, whereas, high tear strength is an advantage especially for the fine margins which help blend the prosthesis into the natural surrounding tissue. The edges of the prostheses are very fine and are pulled regularly while placing the prosthesis. The tear strength of commercially available silicones lies between 5 and  $17 \text{ kNm}^{-1}$ .<sup>20</sup>

The major components of any silicone elastomer are PDMS base, filler, cross-linker, and catalyst. PDMS base is a mixture of vinyl end blocked polydimethylsiloxane chains. These chains are cross-linked together by a hydride function cross-linker. The degree of cross-linking affects the properties of the silicone formed. For example, a high degree of cross-linking results in an inelastic, brittle material, while low cross-link degree produces a weak material with low tear and tensile strength.<sup>13</sup> The mixture of long and short PDMS chains gives a broader bimodal network. This network helps in achieving a combination of good mechanical properties such as tear and tensile strength.

Previous work has shown that a combination of 2 different chain length PDMS results in the best mechanical properties.<sup>13,20</sup> Bellamy et al from Cardiff University, UK used V46 long and V21 short chain PDMS polymers for the development of M511, the most widely used commercial silicone in Europe.<sup>13</sup> V46 (long chains), V31 (medium length chains), and V21 (short chains) PDMS were chosen for this work. Their ratios helped optimize the tear strength. The addition of low molecular weight polymer produced broader molecular weight distribution

and resulted in local high cross-link density between relatively long chains. The extra cross-links from low molecular weight polymer tightened the cross-link network, while longer chains maintained flexibility. The results show that a low concentration of short chains tear strength was optimized while at higher concentrations tear strength was reduced. This is because at higher concentrations of low molecular weight polymer, the cross-link network is tightened to such an extent that the flexibility is reduced and more brittle specimens with reduced tear strength are produced. The combinations of 3 PDMS chains resulted in a range of elasticity. The formulation of base A with 5% cross-linker was most elastic, while base D with 2.5% cross-linker was most brittle. Similar results were observed by Aziz et al<sup>12</sup> when they diluted PDMS long chains C50 with short chains; the strength decreased gradually with increasing short chain content.

Fillers are added to silicones to modify their surface, optical, and mechanical properties. Incorporating filler increases the strength of silicone, and the smaller particle size of fillers results in a high surface area, which, in turn, prevents the incorporation of water.<sup>13</sup> An increase in the filler content would increase hardness and tear strength, but mixing silicone elastomers becomes difficult beyond 20% filler loading. This percentage of filler (20% w/w) was chosen because previous work carried out by Aziz et al<sup>12</sup> showed the effect of increasing filler loading on tear strength. They observed an insignificant difference in the tear strength of formulations with 0% to 15% filler but a significant rise in strength when the filler content increased from 15% to 20%. There was further increase in strength with 25% filler loading, but these formulations proved very difficult to mix.

In the first instance, a heat catalyst was shown to have no effect on mechanical properties and only on the polymerization reaction (Personal communication, Mark Waters, Technovent Ltd, 2015). With the heat catalyst, longer working times of around 30 minutes or even more can

be achieved, while with some formulations containing RTV catalyst, working times can be as short as a few seconds. A heat catalyst was thus chosen for ease of workability.

The results generally indicate an initial increase and then a decrease in strength of the test specimens with increasing cross-linker concentration. One reason for the initial increase could be that more cross-links are formed, thus increasing cross-link density. However, after reaching a peak value, no more cross-linking sites are available, and the residual unreacted cross-linker remains in the silicone. This residual cross-linker mimics the effect of short, low molecular weight, chains and thus decreases the hardness, tensile, and tear strength of the specimens.

The trouser-tear test specimens showed more stretching behavior rather than tearing, while the tensile test specimens failed as expected (Fig. 4). Ideally a tear should extend with the axial strain applied, but most of the specimens stretched.<sup>20</sup> The tear did not extend in the direction of the cut but curled back to form a keyhole (Fig. 4). A representative graph is shown in Figure 5. M511, when tested, also showed similar behavior. This may be due to the anisotropic nature of silicone specimens as the cross-linked network is not symmetric in all directions. Because of the 3 different size PDMS chains and their cross-linking during the polymerization process, an asymmetric network is formed. Hence, the tear cannot follow a straight path of fault lines, resulting in this irregular tear pattern. In addition, the long chains of PDMS aid in stretching before any cross-linking is broken or torn.

The mechanical testing result values of these formulations are comparable with the values obtained for the current commercial silicones, M511 and Z004. The formulation of base A with 5% cross-linker was found to have the optimal tensile and tear strength and would therefore be used for further development of a 2-component RTV silicone suitable for printing. After the optimization of PDMS chains and cross-linker, the focus will be on changing the polymerization

mechanism to RTV for 3D printing and also working out viscosities suitable for 3D printing. The components of silicone will be divided into a 2-component system to be printed in a controlled mechanism with a 3D printer. Moreover, the 3D printing of silicone will be printing layers of silicone but they will not be polymerizing individually. Rather 1 layer would meld into the other to create bulk polymerization and properties would not be different layer by layer.

## **CONCLUSION**

The mechanical properties vary with the different chain length PDMS and cross-linker concentration. A combination of PDMS chains with 5% cross-linker showed optimal results and was chosen for further development of the 2-component RTV silicone. Furthermore, to make the silicone printable the heat catalyst must be replaced with the RTV catalyst with the addition of a moderator and thixotropic agent.

## REFERENCES

1. Wolfaardt J, Sugar A, Wilkes G. Advanced technology and the future of facial prosthetics in head and neck reconstruction. *Int J Oral Maxillofac Surg* 2003;32:121-3.
2. Kanter JC. The use of RTV silicones in maxillofacial prosthetics. *J Prosthet Dent* 1970;24:646-53.
3. Lontz JF. State-of-the-art materials used for maxillofacial prosthetic reconstruction. *Dent Clin N Am* 1990;34:307-25.
4. Maller US, Karthik K, Maller SV. Maxillofacial prosthetic materials-past and present trends. *J Ind Acad Dent Spec* 2010;1:25-30.
5. Eggbeer D, Bibb R, Evans P, Ji L. Evaluation of direct and indirect additive manufacture of maxillofacial prostheses. *Proc Inst Mech Eng H* 2012;226:718-28.
6. Huber H, Studer SP. Materials and techniques in maxillofacial prosthodontic rehabilitation. *Oral Maxillofac Surg Clin North Am* 2002;14:73-93.
7. Bibb R, Eggbeer D, Evans P. Rapid prototyping technologies in soft tissue facial prosthetics: current state of the art. *Rapid Prototyping J* 2010;16:130-7.
8. De Crescenzo F, Fantini M, Ciocca L, Persiani F, Scotti R. Design and manufacturing of ear prosthesis by means of rapid prototyping technology. *Proc Inst Mech Eng H* 2011;225:296-302.
9. Subburaj K, Nair C, Rajesh S, Meshram SM, Ravi B. Rapid development of auricular prosthesis using CAD and rapid prototyping technologies. *Int J Oral Maxillofac Surg* 2007;36:938-43.
10. van Noort R. The future of dental devices is digital. *Dent Mater* 2012;28:3-12.
11. Ratner BD, Hoffman AS, Schoen FJ, Lemons JE. *Biomaterials science*. 3rd ed. London:Elsevier; 2012. p. 1106-16.

12. Aziz T, Waters M, Jagger R. Development of a new poly(dimethylsiloxane) maxillofacial prosthetic material. *J Biomed Mater Res B Appl Biomater* 2003;65:252-61.
13. Bellamy K, Limbert G, Waters MG, Middleton J. An elastomeric material for facial prostheses: synthesis, experimental and numerical testing aspects. *Biomater* 2003;24:5061-6.
14. Wolfaardt JF, Chandler HD, Smith BA. Mechanical properties of a new facial prosthetic material. *J Prosthet Dent* 1985;53:228-34.
15. Symes MD, Kitson PJ, Yan J, Richmond CJ, Cooper GJ, Bowman RW et al. Integrated 3D-printed reactionware for chemical synthesis and analysis. *Nat Chem* 2012;4:349-54.
16. International Organization for Standardization. ISO 37:2011. Rubber, vulcanized or thermoplastic - Determination of tensile stress-strain properties. Available at: <http://www.iso.org/iso/prods-services/ISOstore/store.html>. Accessed January 26, 2016.
17. International Organization for Standardization. ISO 34-1:2015. Rubber, vulcanized or thermoplastic - Determination of tear strength - Part 1: Trouser, angle and crescent test pieces. Available at: <http://www.iso.org/iso/prods-services/ISOstore/store.html>. Accessed January 26, 2016.
18. International Organization for Standardization. ISO 868:2003. Plastics and ebonite - Determination of indentation hardness by means of a durometer (Shore hardness). Available at: <http://www.iso.org/iso/prods-services/ISOstore/store.html>. Accessed January 26, 2016.
19. Cox N. Graphics (and numerics) for univariate distributions. In United Kingdom Stata Users' Group Meeting; 2012.Sep 22 (No. 06).Available at: <http://www.stata.com/meeting/uk12/abstracts/>. Accessed January 26,2016.
20. Aziz T, Waters M, Jagger R. Analysis of the properties of silicone rubber maxillofacial prosthetic materials. *J Dent* 2003;31:67-74.



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**TABLES**

Table 1. Polymer mixtures with fillers (Technovent Ltd)

<b>Vinyl End Blocked PDMS</b>	<b>Formulation</b>
V46 (MW 117000 Da) with 20% wt/wt surface treated silica filler	X
V31 (MW 28000 Da) with 20% wt/wt surface treated silica filler	Y
V21 (MW 6000 Da) with 20% wt/wt surface treated silica filler	Z

Da=Daltons

Table 2. Composition of bases

<b>Base</b>	<b>Combination of PDMS chains</b>	<b>Average Molecular Weight (kDa)</b>
<b>Base A</b>	70% X + 20% Y + 10% Z	29.4
<b>Base B</b>	60% X + 30% Y + 10% Z	26.4
<b>Base C</b>	60% X + 20% Y + 20% Z	25.7
<b>Base D</b>	50% X + 20% Y + 30% Z	22.0

Da=Daltons

Table 3. Summary of ANOVA

<b>Variable</b>	<b>n</b>	<b>Factor</b>	<b><i>df</i></b>	<b>F</b>	<b><i>P</i></b>
<b>Tear</b>	<b>200</b>	<b>Base</b>	<b>3</b>	<b>76.63</b>	<b>&lt;.001</b>
		<b>Crosslink</b>	<b>4</b>	<b>25.52</b>	<b>&lt;.001</b>
		<b>Base#crosslink</b>	<b>12</b>	<b>3.27</b>	<b>&lt;.001</b>
<b>Tensile</b>	<b>200</b>	<b>Base</b>	<b>3</b>	<b>44.04</b>	<b>&lt;.001</b>
		<b>Crosslink</b>	<b>4</b>	<b>21.05</b>	<b>&lt;.001</b>
		<b>Base#crosslink</b>	<b>12</b>	<b>8.34</b>	<b>&lt;.001</b>
<b>Hardness</b>	<b>120</b>	<b>Base</b>	<b>3</b>	<b>316.46</b>	<b>&lt;.001</b>
		<b>Crosslink</b>	<b>4</b>	<b>2181.92</b>	<b>&lt;.001</b>
		<b>Base#crosslink</b>	<b>12</b>	<b>1114.98</b>	<b>&lt;.001</b>

Table 4. Mechanical strength of commercial silicones (M511 and Z004) and formulations with 5% cross-linker. Mean (SD)

	<b>Hardness /Shore A</b>	<b>Tensile strength/MPa</b>	<b>Tear strength /kNm<sup>-1</sup></b>
<b>M511</b>	18.7(0.471)	3.804(0.362)	8.002(0.567)
<b>Z004</b>	30.8(0.373)	5.389(0.740)	9.788(1.846)
<b>Base A</b>	24.3(0.471)	3.524(0.658)	8.484(0.719)
<b>Base B</b>	23.2(0.373)	2.212(0.543)	5.418(1.612)
<b>Base C</b>	24.7(0.471)	2.795(0.311)	5.869(1.506)
<b>Base D</b>	28.5(0.764)	1.463(0.295)	1.274(0.361)

## FIGURES

Fig. 1. Comparison of tensile strength of specimens with different bases and cross-linker concentration.

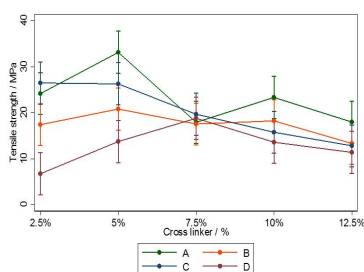


Fig. 2. Comparison of tear strength of specimens with different bases and cross-linker concentration.

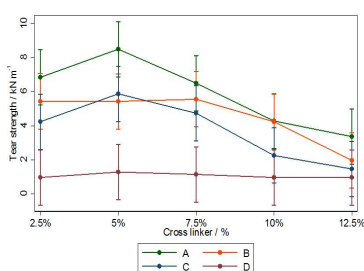


Fig. 3. Comparison of hardness of specimens with different bases and cross-linker concentration.

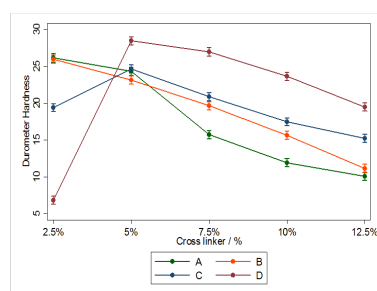


Fig. 4. Tensile and tear test specimens after testing.

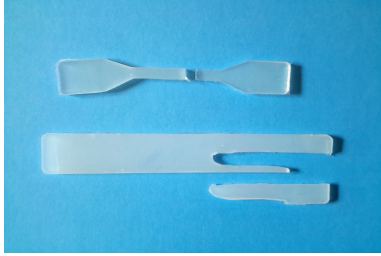


Fig. 5. Tear test graph showing maximum load versus extension.

